CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: DESIGN, SYNTHESIS, AND CHARACTERIZATION OF LOW-COBALT CATHODES

Project ID: BAT251

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Argonne National Laboratory
June 21-23, 2022

2022 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: September 30, 2022
- Percent complete: 90%

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety
  - Cobalt content

Budget

- Total project funding:

  FY22 $4.0M
- ANL, NREL, ORNL, LBNL, PNNL

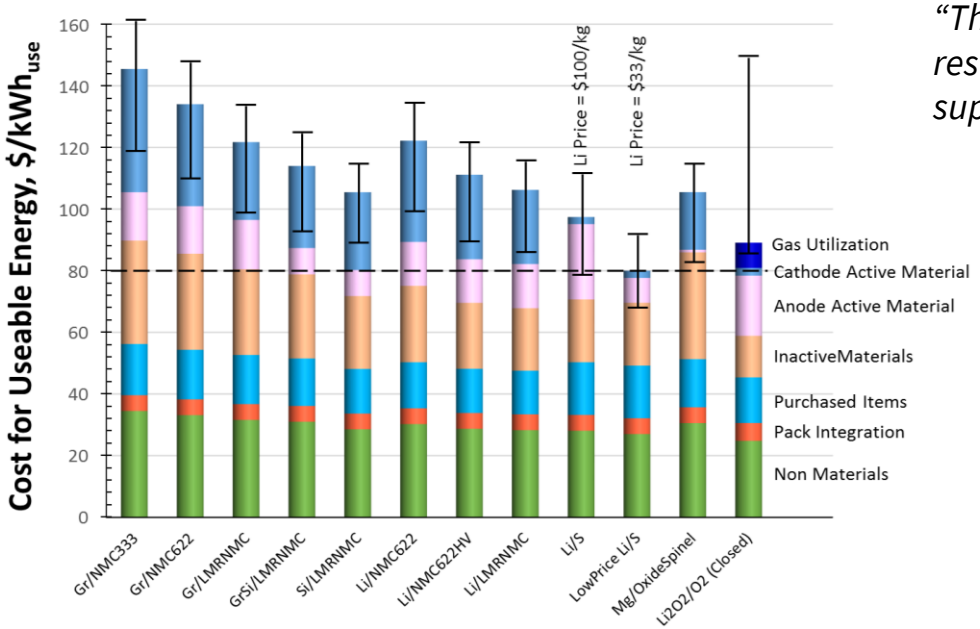
Partners

- ANL, NREL, ORNL, LBNL, PNNL

Students supported from:

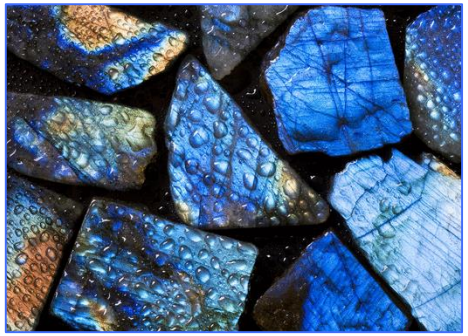
- University of Illinois at Chicago
- University of Rochester
- Oregon State University
- Worcester Polytechnic Institute

Relevance



BatPaC Projected Cost for a 100kWh$_{Total}$, 80kW Battery Pack

"The battery industry uses 42 percent of global cobalt production, while the rest is used in industrial and military applications, and all are competing for supply." – supplychainbrain.com



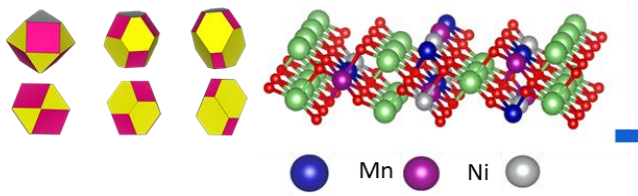
Cost, sustainability, and lack of mature alternatives are the major drivers for continued work in layered transition metal oxides

- Layered transition-metal (TM) oxides represent the best option for near-term advancements for EV batteries
- Li-ion continues to grow and is likely to dominate the market for several decades to come – no guarantees with other technologies (Li-S, "Li-air", multivalent, solid state…)
- Major drivers (safety, energy, power, lifetime, cost) still have room to improve
- ***However, sustainability is a critical factor to the success of the predicted, massive future Li-ion market***

Approach

See also BAT252, 253, 167

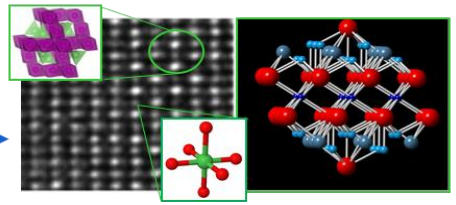
Theory & Models



Atomic-level understanding of the critical roles of cobalt

H. Iddir, G. Chen

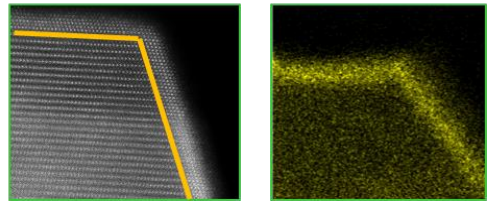
Cathode Design/Synthesis



Implementation of promising cobalt replacement strategies

E. Lee, J. Gim

Surface Stabilization



Design and synthesis of engineered surfaces for high voltage

J. Vaughey, A. Gutierrez

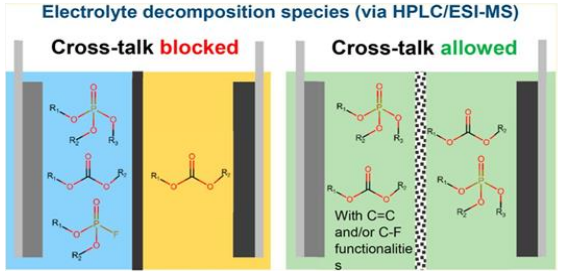
Mechanistic Studies of Critical Issues

Crosstalk, Impedance, Fade…

Coatings, Additives…

Analysis of Modified Cathodes

Full Cell Diagnostics



Understanding mechanisms of cell-level performance & Degradation

D. Abraham, A. Tornheim

Standard Data on all Systems

Electrochemical Analysis

Thermal Properties (DSC)

Gassing Analysis (DEMS)

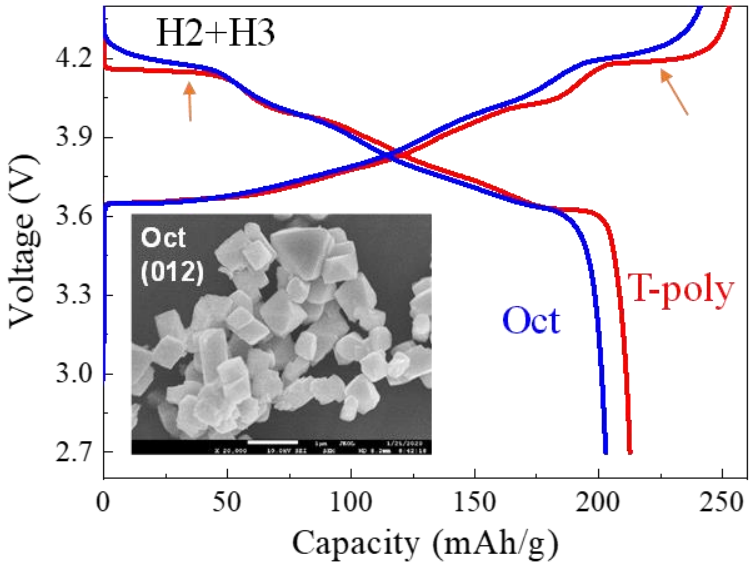
- The team has developed a multi-thrust approach driven by cathode design and synthesis
- Each thrust has two coordinators and works in parallel, on the same materials, as the other thrusts
- All materials tested and characterized according to program protocols to identify promising strategies

Milestones

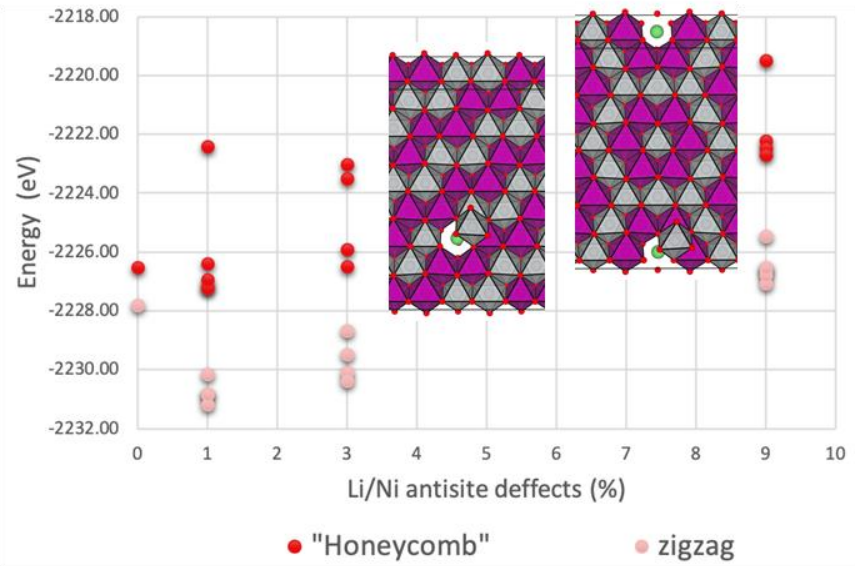
See also BAT252, 253, 167

- *This project seeks to make significant progress towards the realization of cobalt-free, TM-oxide cathodes for next-generation, Li-ion batteries*
- *The goals of cathode design are represented by two prototypical materials*

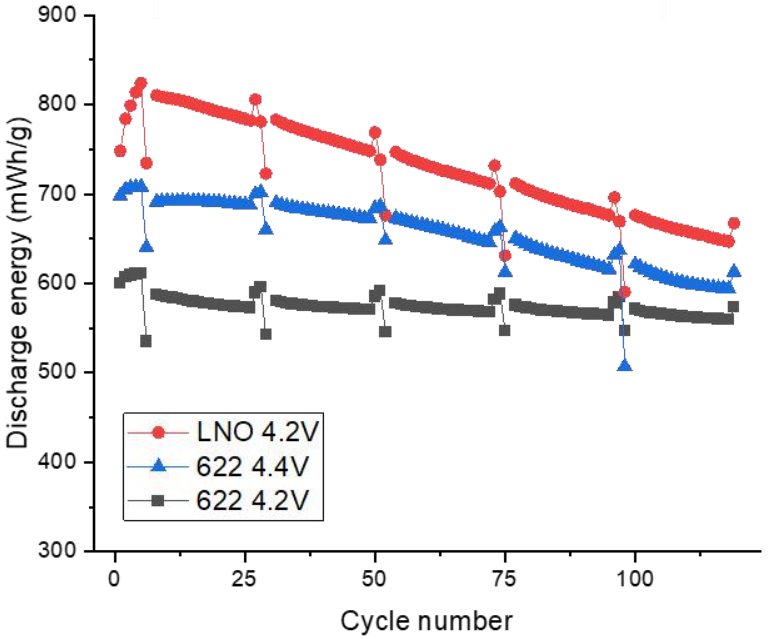
Single Crystal LNO



Ordering and exchange in $Mn_{0.5}Ni_{0.5}$



NMC-622 & LNO metrics



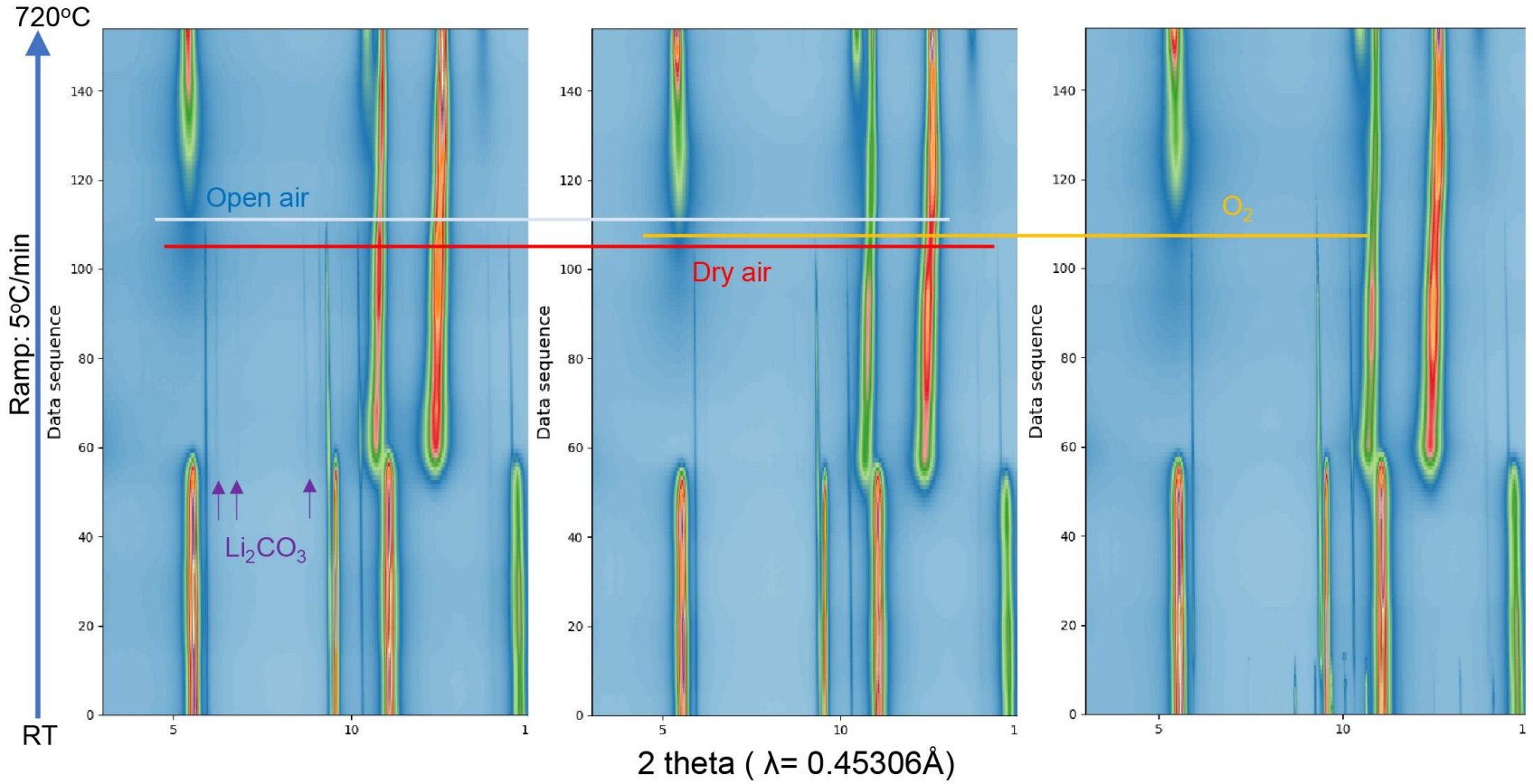
- LNO serves as a physiochemical baseline for understanding the design and properties of high nickel oxides
- $LiMn_{0.5}Ni_{0.5}O_2$ serves as a baseline for understanding the design and properties of 'high Mn', MnNi-based oxides
- NMC-622 serves as a baseline for minimum performance metrics

Technical Accomplishments

$LiNiO_2$: Synthesis-structure-properties

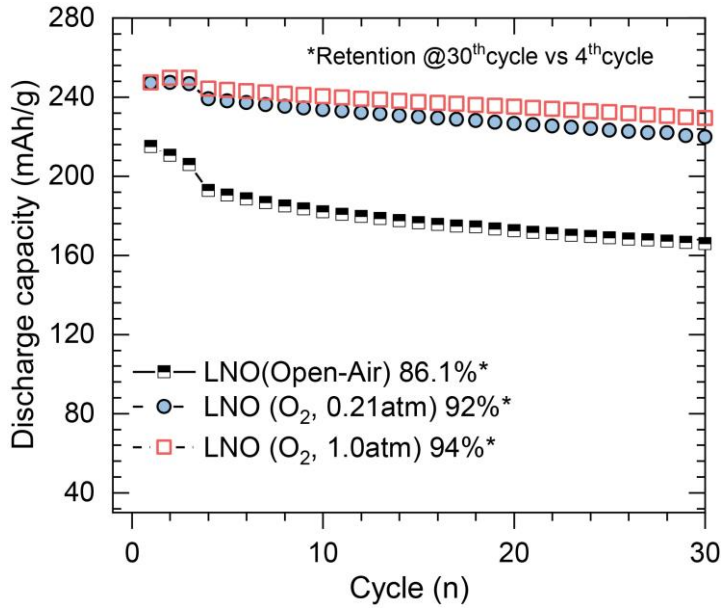
Understanding structure evolution under different atmosphere: pO_2 & moisture

In-situ heating high-energy X-ray diffraction @APS-17BM (Tianyi Li & Wenqian Xu)



Electrochemical performance of LNO (moisture, pO_2)

- 4.3-2.8V, half-cell, Gen2 (1C=200mA/g)
- 3 formation cycles @C/10
- Cycling: C/10 charge, C/3 discharge

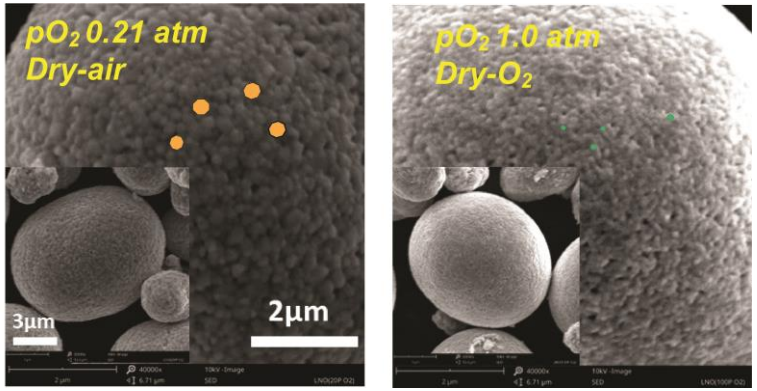


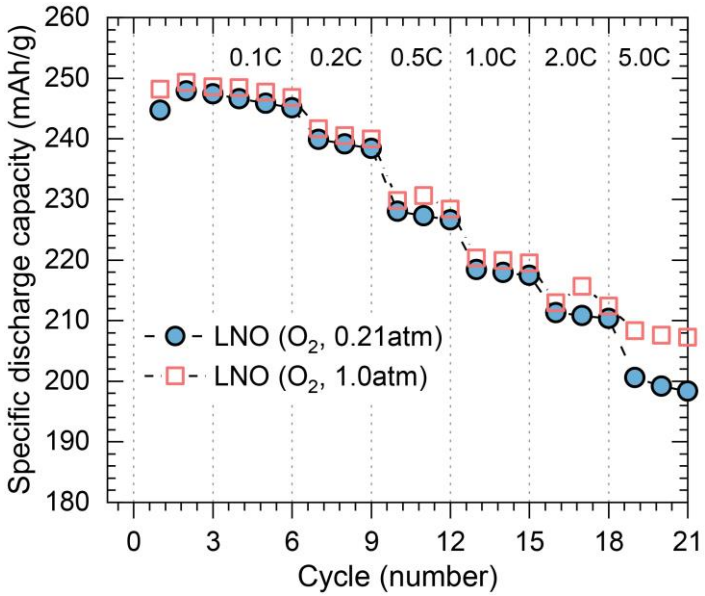
- Li_2CO_3 formation is observed under open-air (moisture, CO_2 rich) heating, while moisture free atmosphere hinders the reaction.
- Hence, the structural evolution to layered $R\bar{3}m$ is delayed due to suppressed lithiation in the presence of moisture; higher melting point of Li_2CO_3 (723°C) than LiOH (462°C)
- Open-air synthesis of LNO results in inferior performance while the use of different pO_2 (0.2atm vs 1.0atm) shows similar performance regarding specific capacity and cycle life.

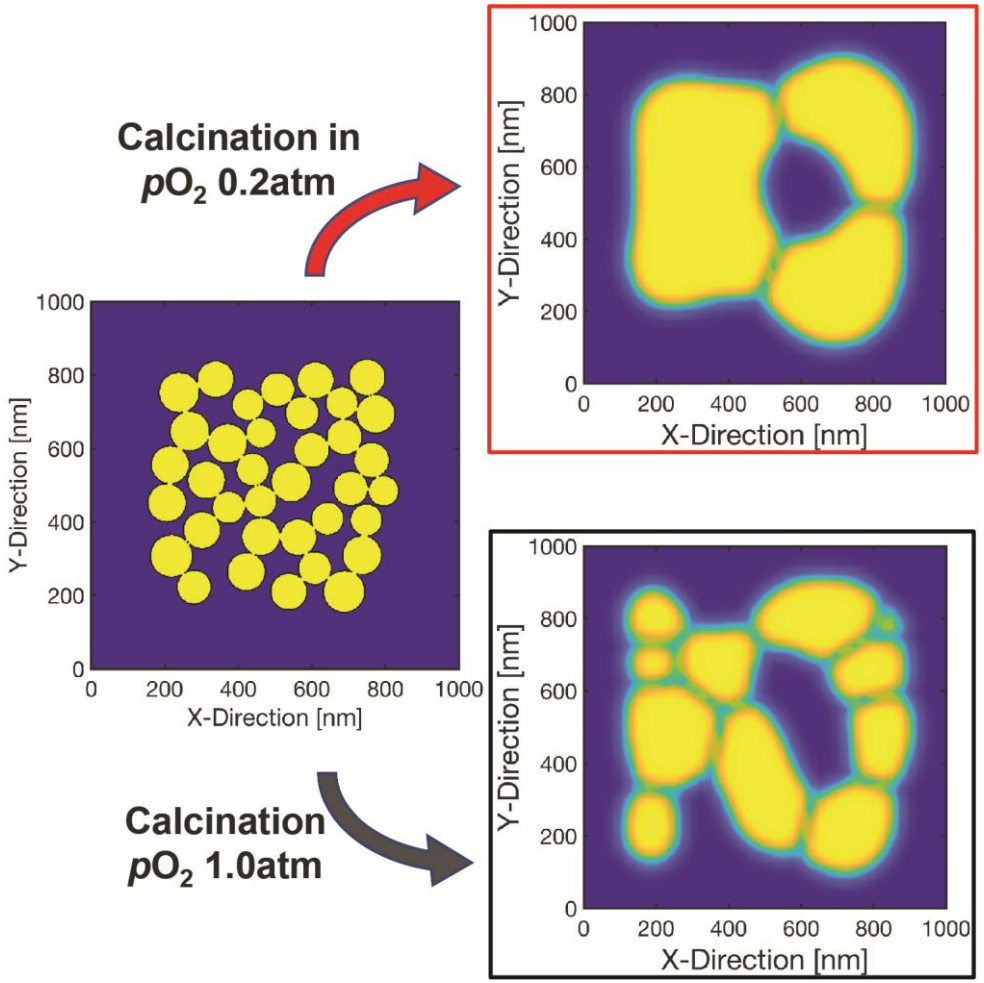
Technical Accomplishments

$LiNiO_2$: Synthesis-structure-properties

Understanding microstructure evolution: Modeling simulation for the influence of oxygen partial pressure



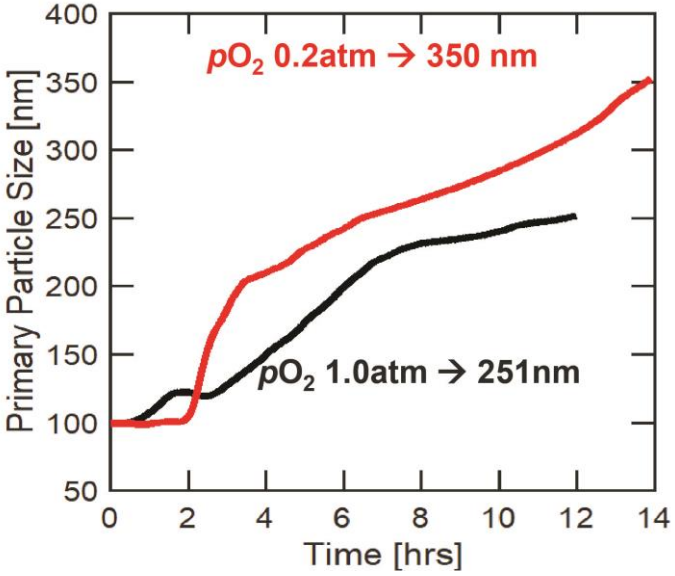




see also BAT402

Pallab Barai, Venkat Srinivasan (ANL)

Average primary particle size



- Primary particle size increases as pO_2 decreases (kinetics between crystal growth and lithiation)
- Smaller primary particle size (higher pO_2) leads to slightly better rate performance as rate increases
- For LNO cathodes, higher oxygen partial pressures help to lithiate the Ni-hydroxide precursor while limiting the growth of primary particle size

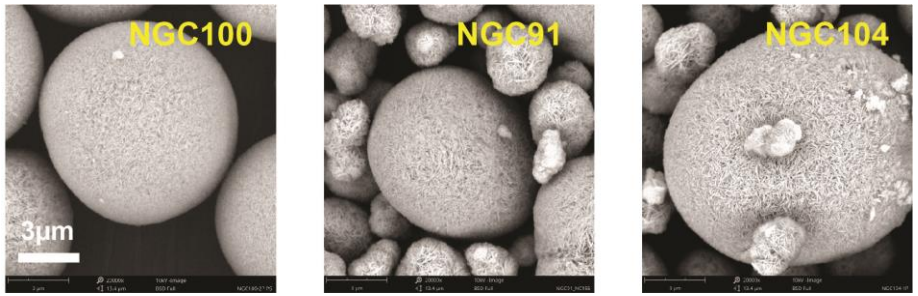
Technical Accomplishments

$LiNiO_2$: A real impact of dopant

Understanding the true role of dopants (Co and Mn): Synthesis condition (temperature tolerance)

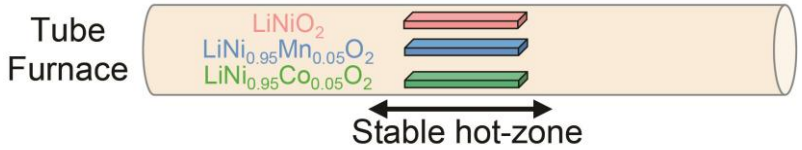
see also BAT167

Composition	Precursor (MERF)*	D50 (µm)	Tap density (g/cc)	BET (m^2/g)
$Ni(OH)_2$	NGC100	9.36	1.94	16.43
$Ni_{0.95}Co_{0.05}(OH)_2$	NGC91	11.99	1.98	N/A
$Ni_{0.95}Mn_{0.05}(OH)_2$	NGC104	6.65	1.56	13.10

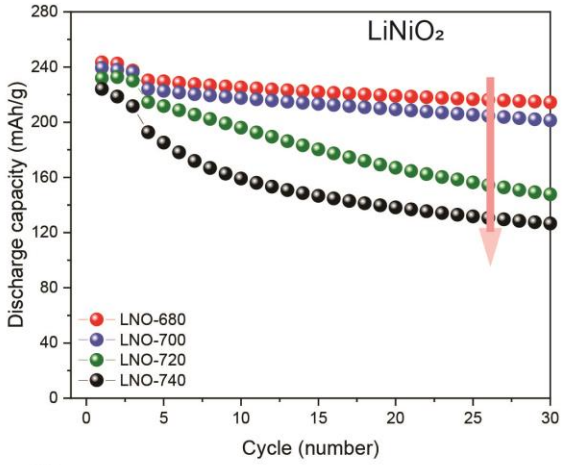


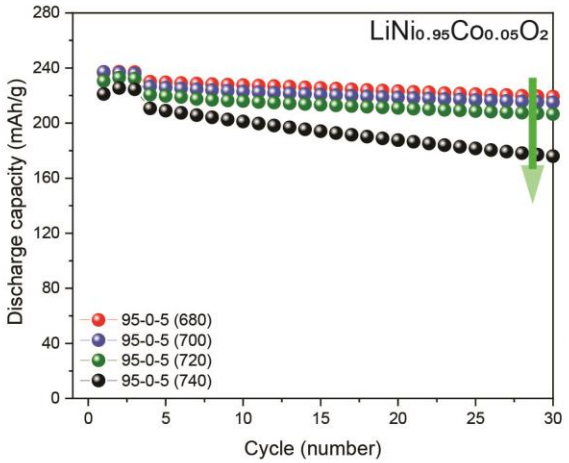
Calcination conditions

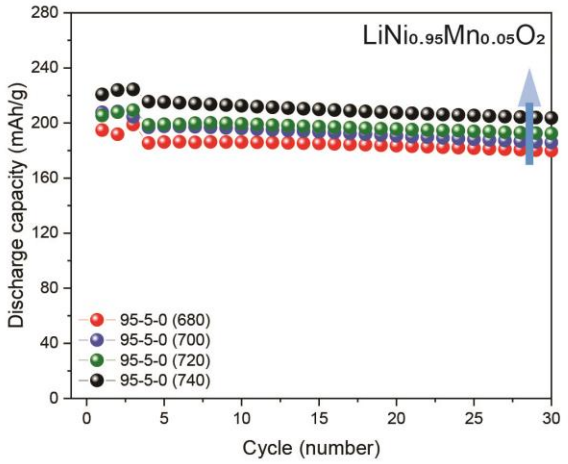
- Lithium hydroxide monohydrate as lithium source
- Li/Metal: 1.02 for all compositions
- Oxygen tube furnace, 2°C/min ramp, 12hr hold
- Calcination carried out at the same time.

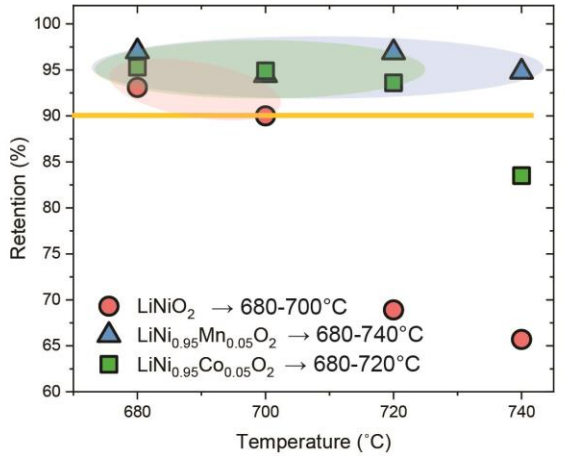


- 4.2-2.8V, Half-cell, Gen2, 3-formation cycles @c/10, cycling @c/10charge, @c/3discharge







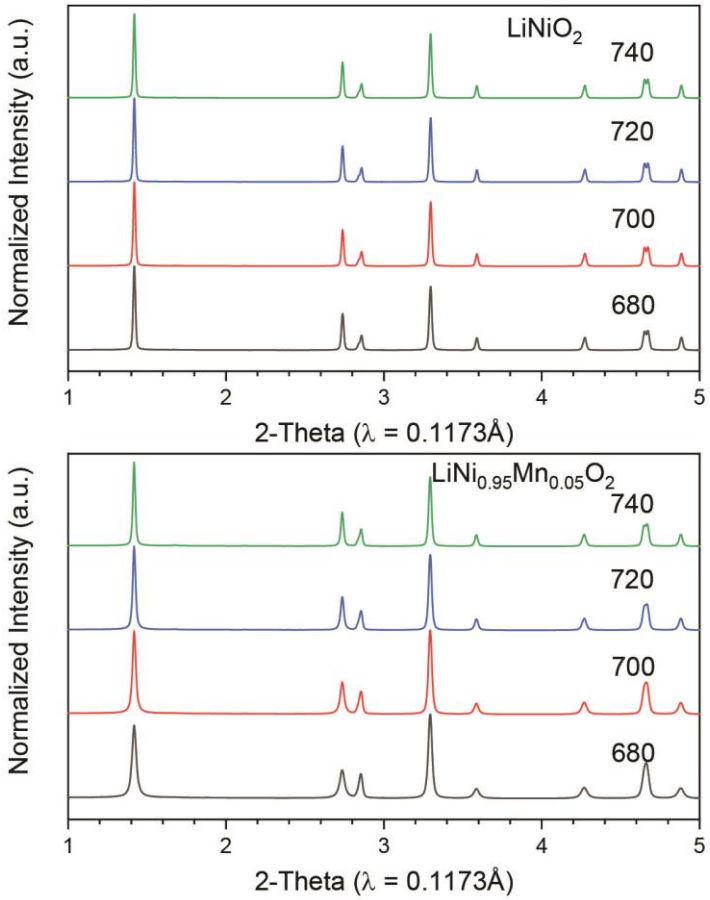


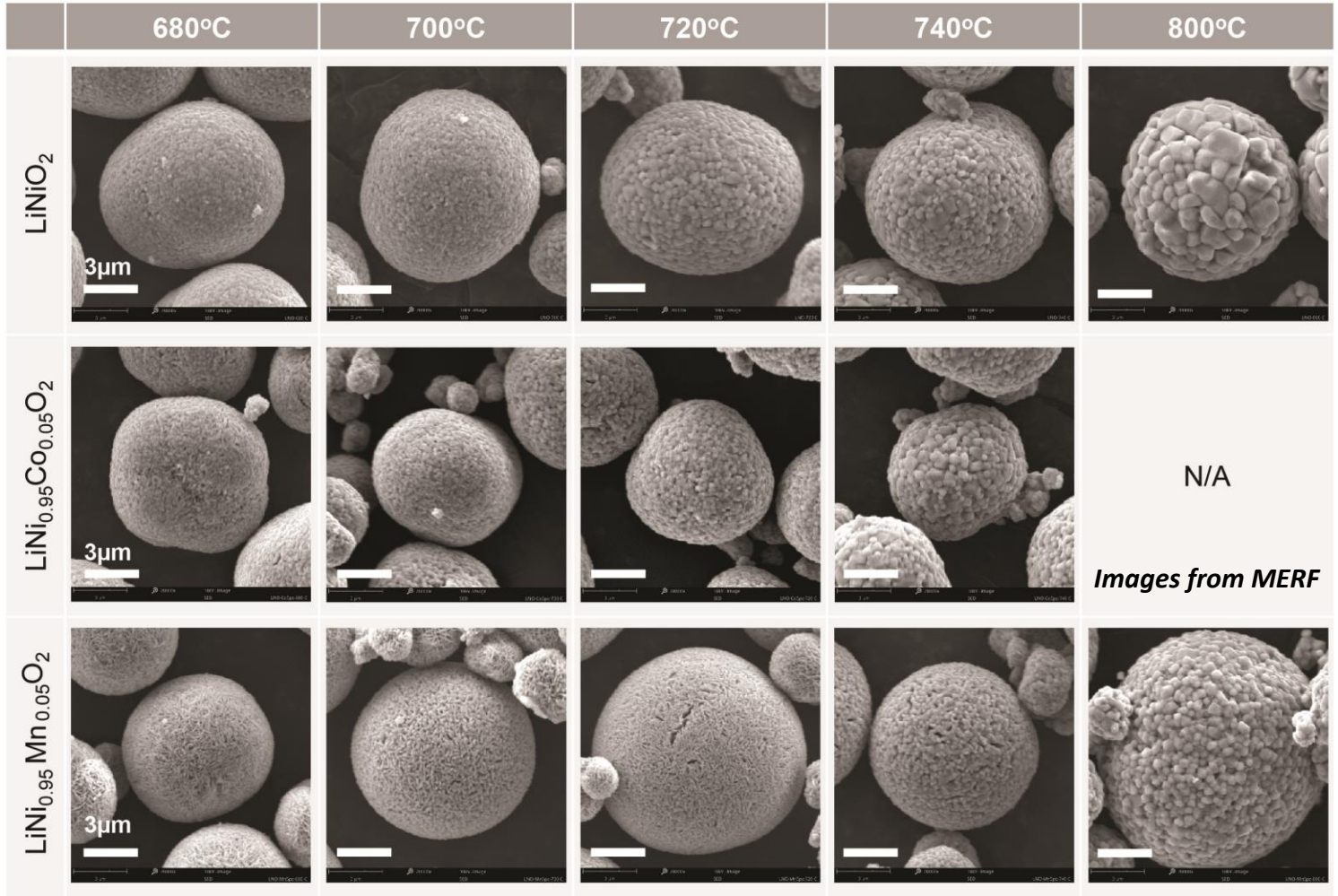
- Screening the effect of calcination temperature (under pure oxygen) for LNO and its derivatives with Mn/Co 5% substitution.
- Mn substitution in LNO expands the range of calcination temperatures in which good performance can be obtained, thereby alleviating, to some extent, the critical dependency on temperature in large-scale calcination

Technical Accomplishments

$LiNiO_2$: A real impact of dopant

Understanding the true role of dopants (Co and Mn): Synthesis conditions (temperature tolerance)





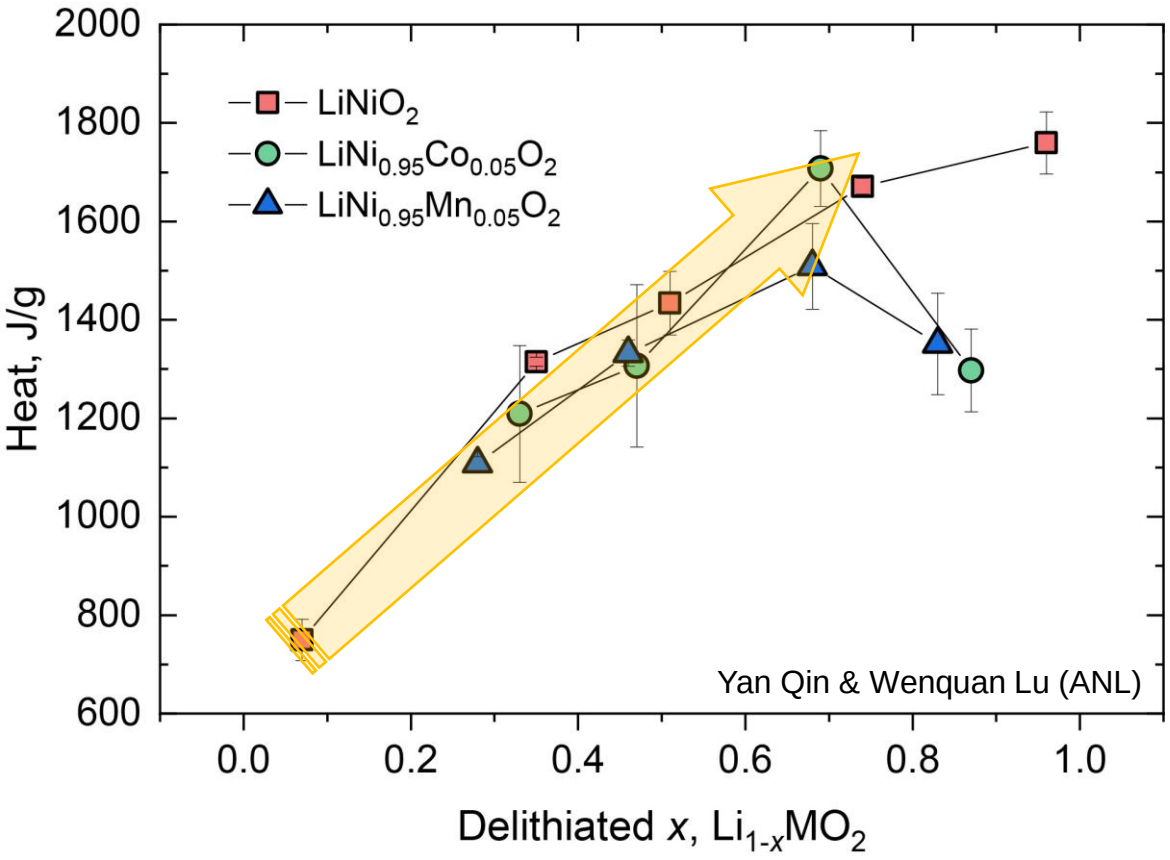
- No significant difference in structure from HEXRD (APS @11 ID-C) or unwanted impurities were observed
- As calcination temperature increases, primary particle sizes increase accordingly, attributed to increased crystallinity increase
- Mn-substituted LNO tends to have smaller grain sizes, while Co-doped LNO shows a similar trend as pure LNO

Technical Accomplishments

$LiNiO_2$: A real impact of dopant

Understanding the true role of dopants (Co and Mn): A benefit beyond expanding synthesis condition

DSC (Differential Scanning Calorimetry) condition
- 3 formation cycles, 3-4.3V at C/10 (1C=200mA/g)
- Charge to 3.7, 3.85, 4.1 and 4.3V.
- DSC scan rate: 5°C/min

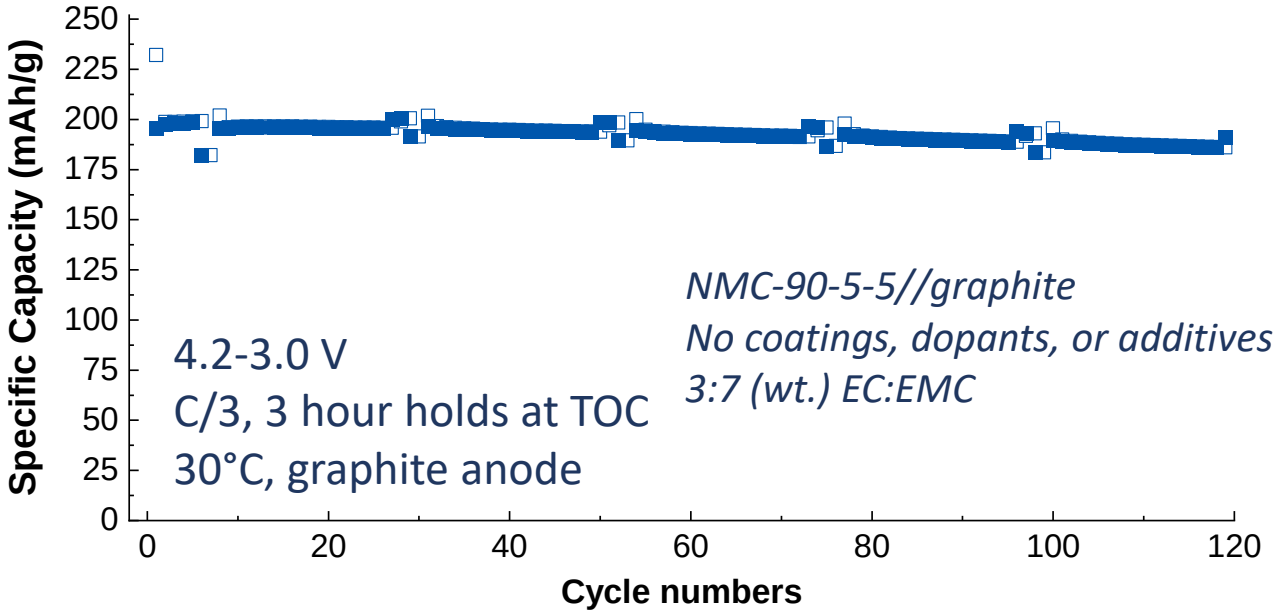


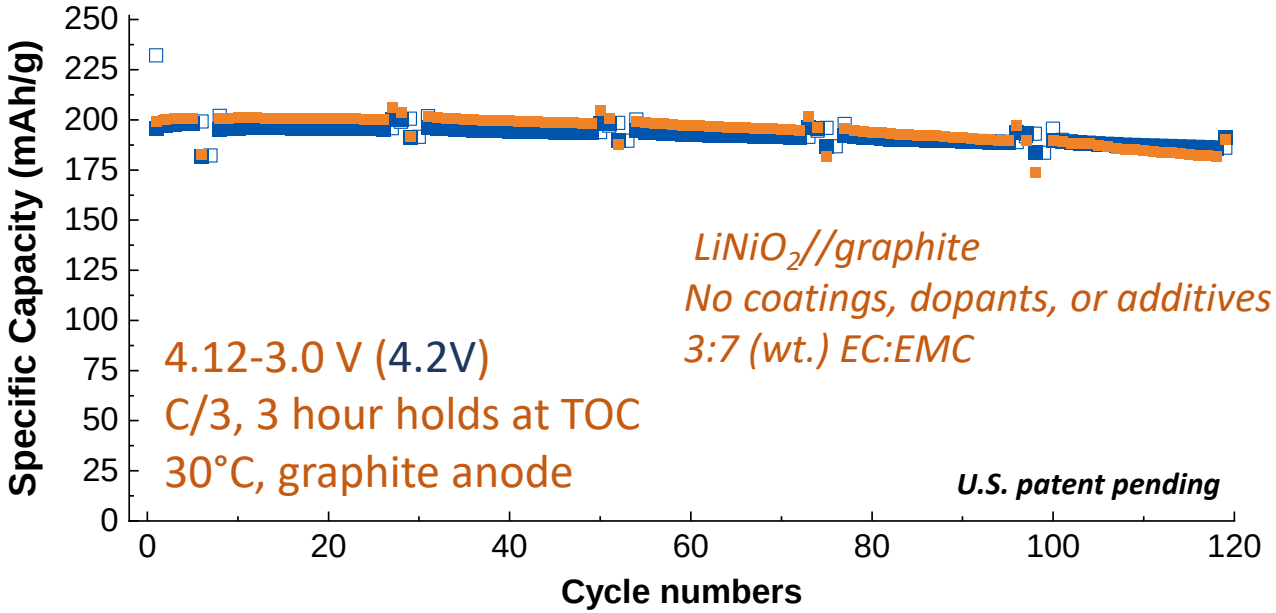
- Optimized LNO and its derivatives with 5% substitution (Co and Mn) was used for thermal stability study (DSC).
- In general, the total heat generation increases as SOCs increase despite which dopant is incorporated in LNO.
- However, doped LNO samples have the maximum heat occurs at 4.1V and 4.3V is out of the trend, probably due to thermal stability dependance of the structure of highly delithiated states.

Expected thermal runaway reaction; (i.e., $Li_{1-x}MO_2$, x=0.1)

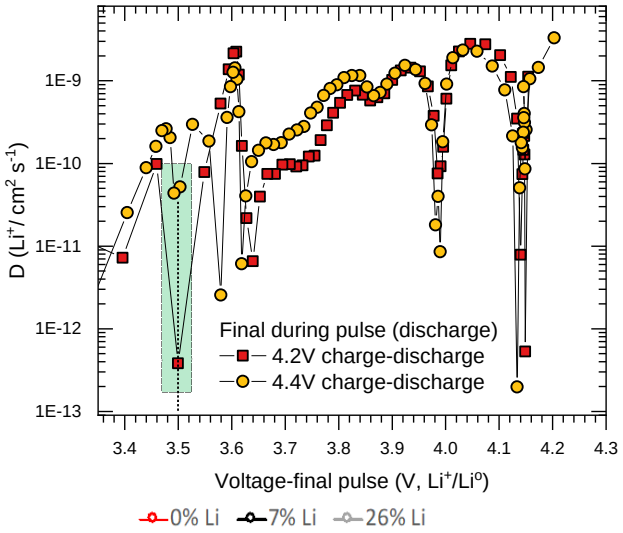
- 1st step: layered → disordered spinel
  $Li_{0.1}(M^{3.9+})_{1.0}O_2$ (layered, $R\bar{3}m$) → $\frac{11}{30}\{Li_{3/11}(M^{2.84+})_{30/11}O_{4.0}\}$ (spinel, $Fd\bar{3}m$) + $\frac{4}{15}O_2 \uparrow$
- 2nd step: disordered spinel → disordered rock-salt
  $\frac{11}{30}\{Li_{3/11}(M^{2.84+})_{30/11}O_{4.0}\}$ (spinel, $Fd\bar{3}m$) → $\frac{11}{30}\{Li_{3/11}(M^{2.84+})_{30/11}O_{3.0}\}$ (rock-salt, $Fm\bar{3}m$) + $\frac{11}{60}O_2 \uparrow$
- Higher Ni, larger amount of unstable Ni^{4+} → more Ni^{4+} migration → pulling down the onset temperature; higher heat generation at the same voltage; rock-salt forms at higher T.
- Mn-doped LNO case: stable MnO_2 framework (higher activation barrier of Mn-migration → lower heat generation.

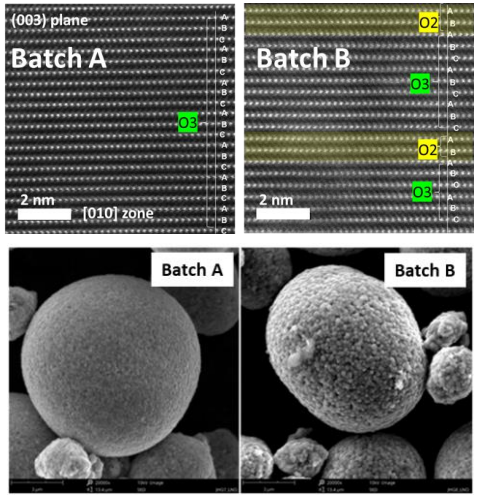
Technical Accomplishments

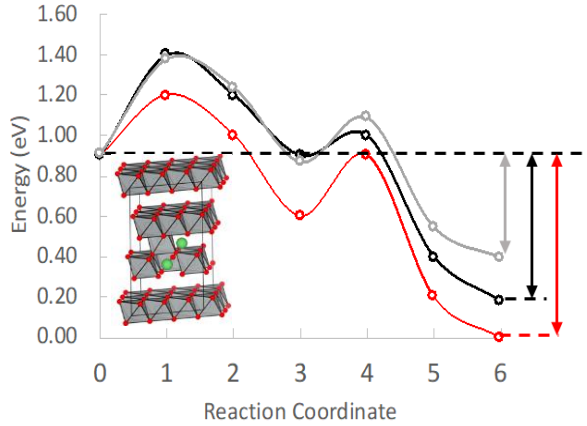


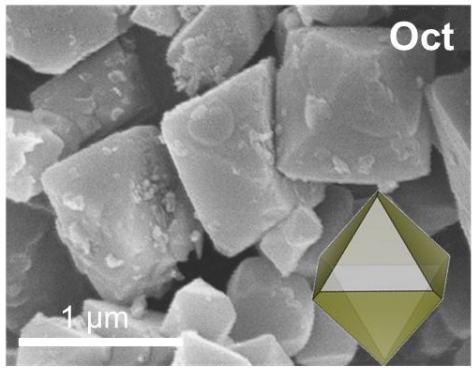


Insight into synthesis-structure-property relationships are leading to enhanced performance of very high Ni-content cathodes









see also BAT253

H. Iddir, J. Garcia (ANL), G. Chen (LBNL)

The stability of LNO-based electrodes, as compared to Ni-rich/doped counterparts, can be greatly enhanced through process control alone

Summary

Influence of pO_2 / moisture of $LiNiO_2$ synthesis

- LNO-based cathodes benefit from high purity O_2 gas for synthesis due to increased kinetics in the lithiation of Ni-hydroxide precursors, smaller primary particle sizes, and enhanced rate capability
- The effect of pO_2 on LNO synthesis is not as significant to structure and performance as is temperature and the presence of moisture
- The presence of moisture during calcination degrades the structure and performance of LNO due to the formation of a Li_2CO_3 intermediate phase and a delay in lithiation of the Ni-hydroxide to higher temperatures

True impact of Mn/Co substitution on $LiNiO_2$

- Pure LNO is extremely sensitive to calcination temperatures – the addition of Mn or Co expands the acceptable range of temperatures in which good structure and performance can be obtained
- When compared over similar states of charge, pure LNO from this project performs on par with substituted derivatives, such as 90-5-5, this has been accomplished through a deeper understanding of synthesis and processing conditions and the resulting physical and electrochemical properties
- A general trend between the SOC and thermal stability was observed for $LiNi_{0.95}M_{0.05}O_2$ (M=Co and Mn) and $LiNiO_2$, where Mn/Co substitution showed some benefit with regards to thermal stability at high SOCs, studies are ongoing

Future Work

- Exploration, development, and fundamental understanding of new processes for tailoring the surface and bulk of LNO-based cathode oxides
- Fundamental studies on the true mechanistic impacts of other dopants such as Mg, Al, Fe and the like, utilizing our highly-optimized LNO as a new baseline
- Collaborations with the Theory and Modelling team to understand dopant site-selectivity related to process conditions
- Larger-scale electrochemical testing of most promising systems

All future work is subject to change depending on funding levels

Collaboration and Coordination

Next-Gen Cathode Project Contributors

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- David Wood
- Zhenzhen Yang
- Junghoon Yang
- Jianzhong Yang
- Haotian Zheng
- Lianfeng Zhou
- Peng Zuo

Major Research Facilities

- Materials Engineering Research Facility
- Post-Test Facility
- Cell Analysis, Modeling, and Prototyping
- Spallation Neutron Source
- Environmental Molecular Sciences Laboratory
- Advanced Light Source
- Battery Manufacturing Facility
- Advanced Photon Source (APS)
- Laboratory Computing Resource Center (ANL)
- NMR Spectroscopy Lab (ANL)
- National Energy Research Scientific Computing Center (LBNL)
- Stanford Synchrotron Radiation Light Source

Support for this work from the ABR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Peter Faguy, David Howell

Response to Previous Year's Reviewer Comments

This project was not reviewed